

$$\begin{aligned}
 &U(f_1 + f_2 + \dots + f_{n+1}) - \sum_{r=1}^{n+1} U(f_1 + \dots + f_{r-1} + f_{r+1} + \dots + f_{n+1}) + \\
 &\sum_{r=1}^n \sum_{s=r+1}^{n+1} U(f_1 + \dots + f_{r-1} + f_{r+1} + \dots + f_{s-1} + f_{s+1} + \dots + f_{n+1}) \\
 &\dots + (-1)^{n+1} U(0) = 0
 \end{aligned}$$

identically. If $U(f)$ is also homogeneous, the functional defined by the equation

$$W(f_1, f_2, \dots, f_n) = U(f_1 + \dots + f_n) - \sum_{r=1}^n U(f_1 + \dots + f_{r-1} + f_{r+1} + \dots + f_n) + \dots + (-1)^n U(0)$$

is easily proved to be linear in each of its arguments. If $f_i = f_2 = \dots = f$, it follows from definition and the condition of homogeneity, that

$$W(f, f, \dots, f) = K_n U(f),$$

where

$$K_n = \sum_{r=0}^{n-1} (-1)^r \frac{n(n-1) \dots (n-r+1)}{r!} (n-r)^n$$

But this expression can be proved equal to $n!$ which cannot vanish for any positive value of n , and since the n -linear functional W can be expressed as a multiple Stieltjes integral the homogeneous functional $U(f)$ of order n can be put in the same form.

¹ Riesz, *Ann. Sci. Ec. norm., Paris*, (Ser. 3), 28, 1911, (36-43).

² *Ibid.*, 31, 1914, (9-14).

³ Fréchet, *New York, Trans. Amer. Math. Soc.*, 16, 1915, (215-234).

THE CRYSTAL STRUCTURE OF CHALCOPYRITE DETERMINED BY X RAYS

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Introduction.—This investigation of the atomic structure of crystals of chalcopryrite (CuFeS_2) was undertaken, as no study of a complex sulfide by the method of X-rays had previously been carried out. Moreover, comparatively few crystals of the tetragonal system, in which chalcopryrite crystallizes, have been examined; the only ones being certain oxides of the formula MO_2 studied by Vegard¹ and by Williams.² Yet the determination of the structure of crystals belong-

ing to other than the isometric system is likely to throw most light on the fundamental factors involved, such as the interatomic forces and the size and shape of the atoms themselves.

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Description of the Apparatus and Procédure.—The method employed was in principle the same as that described by W. H. and W. L. Bragg,³ but the apparatus was modified in several respects.

The electrical equipment for the X-ray excitation consisted of an interrupterless transformer of 20-kilowatts capacity. The X-ray tube was provided with a target of specially purified palladium, 2 mm. thick, silver-soldered onto a copper block, the face of which was set nearly perpendicular to the direction of the cathode rays. The electroscope used was one of the double-tilted form devised by Bumstead.

The crystal used in this investigation was selected from a number kindly loaned us by Prof. C. H. Warren of the Massachusetts Institute of Technology. The crystal was of the sphenoidal type,⁴ approximately 8 mm. on the edges.

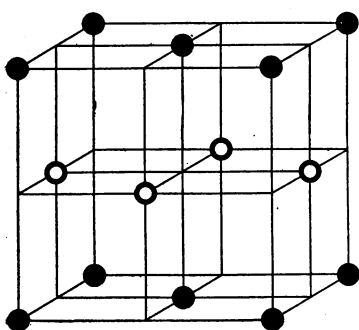
Summary of the Observations.—The following table summarizes the observations. The significance of the 'calculated' angles and intensities will be described below.

TABLE I
SUMMARY OF THE OBSERVED AND CALCULATED RESULTS

CRYSTAL PLANE	ORDER OF REFLECTION	ANGLE OF REFLECTION		ELECTROSCOPE DEFLECTION	RATIO OF INTENSITIES	
		Observed	Calculated		Observed	Calculated
(100)	I	6°25'	6°25'	5.5	100.0	100
	II	12°55'	12°55'	9.0	164.0	217
(001)	I	6°32'	6°32'	13.0	100.0	100
	II	13° 9'	13° 8'	33.5	256.0	222
(111)	I	5°32'	5°35'	49.0	100.0	100
	II	11° 7'	11°14'	6.5	13.0	4
	III	16°33'	16°58'	4.0	8.0	7
(11 $\bar{1}$)	I	5°41'	5°35'	69.0	100.0	100
	II	11°26'	11°14'	10.0	14.0	4
(110)	I	9° 7'	9° 6'	190.0	100.0	100
	II	18°28'	18°27'	45.0	24.0	20
	III	27°52'	28°19'	11.0	6.0	7
(1 $\bar{1}$ 0)	I	9° 4'	9° 6'	61.0	100.0	100
	II	18°23'	18°27'	29.0	47.0	20
(101)	I	9° 7'	9°10'	200.0	100.0	100
	II	18°29'	18°35'	50.0	25.0	20
	III	28°25'	28°32'	9.0	4.5	7

Interpretation of the Results.—In determining the atomic structure of chalcopyrite, we will first attempt to fix the type of lattice on which it is constructed. For approximate purposes its crystals may be regarded as isometric, since the axial ratio $a : c$ (1 : 0.985) is nearly unity.

The interplanar distance d (that is, the distance between like planes of atoms) is by the fundamental law of reflection ($n\lambda = 2d \sin \theta$) inversely proportional to the sine of the angle of reflection (θ). For the three fundamental planes (100) (101) (111) the angles were $6^\circ 25'$, $9^\circ 7'$, and $5^\circ 32'$. The reciprocals of the sines of these angles stand to one another in the ratio 1 : 0.706 : 1.152. The ratios of the interplanar distances in the three possible types of isometric lattice, known as the cubic, the face-centered, and the cube-centered^b are respectively 1 : 0.707 : 0.573; 1 : 0.707 : 1.146; and 1 : 1.414 : 0.573. The lattice in-



COPPER AND IRON ATOMS IN CHALCOPYRITE LATTICE.

involved in the chalcopyrite crystal is therefore obviously the face-centered type; and we may infer that the heavy atoms, which predominate in determining the reflection, must be the points in this lattice.

Since there is only a small difference in the atomic weights of iron and copper, their reflecting powers, like those of potassium and chlorine in potassium chloride, will not be greatly different. The atoms of iron and copper will therefore be practically indistinguishable in their effect on the X-rays. The observations then show that the basic lattice formed by the iron atoms must intersect that formed by the copper atoms in such a way as to form together a single face-centered lattice.

A study with the aid of a model of possible arrangements by which two different kinds of atoms, present in equal numbers, could together form a single face-centered lattice shows that there is only one such arrangement; namely, that shown in the accompanying figure, in which the iron atoms and copper atoms are represented by the solid and annular circles. It is evident, moreover, from the symmetries of the atomic arrangements that the vertical axis in the figure corresponds to the tetragonal or c axis in the crystal.

These conclusions are corroborated by the fact that the observed angles of reflections agree closely with the 'calculated' angles (given in the table), which were computed geometrically from the assumed loca-

tion of the atoms in the lattice, taking as a basis the observed angle for the (100) plane.

We may now proceed to determine the location of the sulfur atoms, which can be done with the aid of the intensity measurements. It is known that, when the reflection takes place from only one kind of plane, the reflections of the first, second, and third orders have intensities which stand to one another approximately in the ratios 100 : 20 : 7, commonly called the normal intensity-ratios. It is evident, if there be secondary planes of lighter atoms intermediate between the primary planes of heavier atoms giving rise to a given reflection, that the reflection will be diminished or increased in intensity in correspondence with the difference in phase of the two trains of emerging rays waves. In case the secondary planes of atoms lie midway between the primary planes, there would be a phase-difference of half a wave-length for the first order, one wave-length for the second order, and $1\frac{1}{2}$ wave-lengths for the third order; hence there would result a weakening of the intensity of the first-order and third-order reflections (equal for the two orders) and a strengthening of that of the second order. In case the secondary planes are displaced one-fourth of the distance between the primary planes, the phase difference will be $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of a wave-length for the first, second, and third orders, and hence there will be an increase in the intensities of the first order and third orders (equal in the two cases) and a relatively large decrease in the second order.

Let us consider now the relative intensities of the different orders for the different planes. We see that for the (100) plane the ratio of the observed intensities of the first and second orders has the value 100 : 164 in place of the normal one 100 : 20. This large relative weakening of the first order and strengthening of the second order shows that planes of sulfur atoms are located not far from midway between the (100) planes of iron and copper atoms. The reflections from the (001) plane show a similar reversal of the normal ratio; and lead to the corresponding conclusion that planes of sulfur atoms are located also not far from midway between the (001) planes of iron and copper atoms. The form and location of the lattice of sulfur atoms becomes thereby fixed, if we consider the additional fact that the number of sulfur atoms is equal to the number of iron and copper atoms. In the figure given above a sulfur atom would be located at the center of each alternate cube (that is, in four of the eight cubes there represented).

This conclusion is confirmed by the observations of the reflections from the other planes. The geometrical relations show that this location of the sulfur atoms involves that they lie in the (110) and (101)

planes of the iron and copper atoms; and that there is a plane of sulfur atoms in the (111) plane displaced one-fourth of the interplanar distance between the composite planes of iron and copper atoms. Correspondingly, the (110) and (101) planes show the normal ratios of intensities of the reflections for the first, second, and third orders; and the (111) plane shows the required decrease of the second-order reflection, and the expected normal ratio of the first-order and third-order reflections.

The relative intensities of the different orders can be calculated from the principle that the intensity of reflection from a plane of atoms is proportional to the square of the mass per unit-area.⁶ Thus, the intensity of reflection from the (111) sulfur-atom plane would be to that from the (111) composite iron-copper atom plane as $(2 \times 32)^2: (56 + 63.6)^2$,² since there are two atoms of sulfur in an area equal to that in which there is one atom of iron and one atom of copper. The intensity of the resultant reflection will evidently be dependent both on the magnitudes of these two component reflections, and on the difference in phase in which they emerge. Algebraic expressions for the relative resultant intensities of the reflections of the different orders can be readily formulated. With the aid of these expressions the 'calculated' ratios of intensities given in the above table were obtained. It will be seen that there is a striking parallelism between the calculated and observed intensities.

Finally, we may further test the correctness of the deduced atomic structure by calculating the density of the substance and comparing it with the known density. Referring to the figure, it is seen that the space which it represents has associated with it two iron atoms, two copper atoms, and four sulfur atoms, or 2 of the atom-groups CuFeS_2 . Since the mass of the hydrogen atom is 1.64×10^{-24} grams, that of these two CuFeS_2 groups is $2 \times \frac{183.6}{1.008}$ times as great, or 5.972×10^{-22} grams. The volume of the space in question is, however, equal to $8 d^3 \times 0.985$, where d represents the distance between the (100) planes of copper-iron atoms (that between the (001) planes being $0.985 d$). This distance d may be obtained from the law of reflection $\lambda = 2 d \sin \theta$ by substituting for θ the observed angle of reflection ($6^\circ 25'$) for the (100) plane, and by substituting for λ its value 0.584×10^{-8} cm. as determined by W. L. Bragg⁷ for a palladium target. The value of d is thus found to be 2.614×10^{-8} cm., and that of the volume in question 1.407×10^{-22} cm. The calculated density is therefore $5.972/1.407$, or 4.24. The density of the mineral chalcopyrite, according to the

best determinations, lies between 4.1 and 4.3. That of the specimen used in this investigation is 4.19.

¹ Vegard, *Phil. Mag., London*, Nov., 1916 and Jan., 1917.

² Williams, *London, Proc. R. Soc.*, 93, 1917, (418).

³ Braggs' *X-Rays and Crystal Structure*, 1915, (22).

⁴ Dana's *Mineralogy*, Fig. 10, 1892, (81).

⁵ Tutton's *Crystallography*, 1911, (501); or Braggs' *X-Rays and Crystal Structure*, 1915, (91).

⁶ Bragg, *op. cit.*, pp. 120-127.

⁷ Kaye, *X-Rays*, 1917, (226).

THE ISOSTATIC SUBSIDENCE OF VOLCANIC ISLANDS

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Objection has sometimes been made to Darwin's theory of upgrowing coral reefs on subsiding foundations on the ground that the subsidence of the reef foundations should lower the ocean surface and lay bare a belt of recent marine deposits of smooth surface and simple shore line around the continental masses, while as a matter of fact the shore lines of continents are usually more or less embayed, as if the sea had recently advanced upon the unevenly eroded surface of the continental margins. The objection will, however, be found to have small weight when it is seen to rest upon the implied postulate that the embayments of continental coasts have as a rule been produced by a universal rise of the ocean surface, everywhere of the same amount and date, whereas their embayments testify to no such simple origin; and to proceed upon the unwarranted assumption that the subsidence of reef foundations requires the subsidence of broad areas of the ocean floors, whereas the local subsidence of the foundations themselves is all that is necessary. The postulate will first be examined and refuted; the assumption will then be considered and its alternative will be preferred.

The embayment of continental coasts is certainly of widespread occurrence, but when the embayments are closely examined they are found to be of dates and dimensions so diverse that they cannot be explained by a universal rise of the ocean. In the first place, the most pronounced embayments are the fiord coasts of quaternary glaciation; there is good reason to believe that the great troughs of such coasts were scoured out deep below sea level by huge glaciers, and that, far from the ocean having recently risen to submerge the troughs, the coasts have in several fiord regions risen from the ocean, as their elevated shore lines testify; these